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KINETICS OF REACTION BETWEEN SILVER BROMIDE
AND PHOTOGRAPHIC SENSITIZERS

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ABSTRACT

The kinetics of the reactions of silver bromide with sensitizing materials have been studied for comparison with the process of photographic sensitization by the same compounds. Sodium sulphite, reacting with silver bromide to give metallic silver, and allyl thiocarbamide, reacting with it to give silver sulphide, were chosen. The reactions were followed by change in bromide ion concentration. Data on solubility and adsorption were obtained to assist in interpretation of the results. The reaction with allyl thiocarbamide is autocatalytic; under the conditions of the experiments it appears to take place by decomposition of dissolved material at the surface of the silver sulphide. The sulphite reaction is also autocatalytic, and it seems probable, on theoretical grounds, that this is an essential characterist of the sensitization process.

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I. INTRODUCTION

It is now generally conceded that gelatin suitable for making photographic emulsions contains traces of materials which have a specific sensitizing effect. All of those which have been isolated (1)¹ react with silver halides to form silver sulphide, and the numerous compounds which have been patented (2) for use as sensitizers of silver bromide-gelatine emulsions all have this characteristic or else form the analogous silver selenide or telluride. We have recently found (3)

¹ Numbers in parentheses here and throughout the text refer to the references at the end of the paper.

that sodium sulphite is a sensitizer approaching allyl thiocarbamide in effectiveness. The product of its reaction with silver bromide is metallic silver, instead of silver sulphide. While no sensitizers which reduce silver halides to metal have been isolated from gelatin, it is probable that some silver is formed during the normal ripening process.

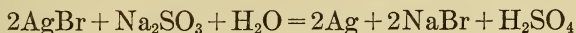
All these compounds almost certainly function by reacting with the silver halide of the emulsion, since they become effective only after digestion of the emulsion with the sensitizer under conditions favoring reaction between them. The silver sulphide or silver which is formed becomes the material of the sensitivity nuclei on the grains. It has been evident from the first discovery of the sensitizers, however, that the formation of silver sulphide or silver in the emulsion is not a sufficient condition for sensitization. It frequently causes only fog, as when silver sulphide is formed by addition of alkali sulphides (1) or when most reducing agents are used. Sheppard (1) pointed out that the compounds covered by his patents all have the common characteristic of forming molecular compounds with silver halides, and postulated that the silver sulphide must be formed by rearrangement of such compounds in order to act as a sensitivity nucleus. Sodium sulphite falls under this classification, since the well-known solubility of silver halides in a solution of sodium sulphite indicates the formation of a complex silver-sulphite ion.

We have studied the kinetics of the reactions between silver bromide and sensitizers with the two-fold purpose of correlating the results with the photographic data and of attempting to find whether a particular reaction mechanism is common to sensitizers. Experiments on this subject have been suspended for lack of funds with the investigation incomplete, but the results which have been obtained are sufficiently promising to warrant publication.

Two sensitizers have been used: sodium sulphite and allyl thiocarbamide. The experiments were carried on under conditions approaching those existing in the emulsion, using a large excess of silver bromide and a low concentration of sensitizer. The progress of the reaction was followed, in both cases, by the change in bromide-ion concentration of the solution. This was determined by the silver-silver bromide electrode, using the apparatus described in a previous communication (4). The method is rapid, convenient, and sensitive. The relative values of bromide-ion activity obtained during a run were correct to about 1 percent, this sensitivity being practically independent of the concentration. The presence of solvents for silver bromide, such as sodium sulphite, allyl thiocarbamide, or ammonia, does not interfere with the working of the electrode provided the solution is saturated with silver bromide. The least unsaturation causes serious error, but the conditions of the reactions, with a large amount of finely divided silver bromide in suspension, insured saturation, and it was found that the electrode responded rapidly enough to give reliable readings even during the progress of the reaction.

II. THE REACTION OF SILVER BROMIDE WITH SODIUM SULPHITE

Sodium sulphite apparently reacts with silver bromide according to the equation



The solid reaction product is silver, and contains no silver sulphide. All experiments were carried out with exclusion of oxygen by passing a current of nitrogen or hydrogen through the solution.² The apparatus was provided with three-way cocks on the inlet and outlet tubes so that sulphite could be introduced and samples removed without admitting air. Samples were caught in thin-walled weighing bottles packed in ice, and rapidly chilled to 30 C, the temperature of the thermostat used for electrode readings of bromide-ion concentrations; at this temperature the rate of reaction was negligible. All reactions were run in the dark room under a Wratten no. 0 safelight, although this precaution was apparently unnecessary.

The first series of reactions was run at $73.4 \pm 0.2^\circ \text{C}$, in unbuffered solutions. All the suspensions contained 0.03 mol AgBr per liter, either without protection or in 1 percent gelatin or 2 percent gum-arabic solution. When unprotected silver bromide was used, it was precipitated and washed just before the reaction. The fresh material was considerably peptized by the sulphite, in the absence of other electrolytes. The results of this series are summarized in table 1. All the reactions were characterized by an induction period, followed by a constant rate of reaction. This constant rate persisted up to a bromide-ion concentration of about $6 \times 10^{-4} N$. The rate of reaction decreased slowly after this in the gelatin suspensions and more rapidly in the unprotected ones. The maximum rate given in the sixth column of the table was characteristic of the reaction over most of the period of a 6-hour run and has accordingly been given as the best measure of the reaction velocity. These rates of reaction are of the right order of magnitude to agree with the analytical data (3, figs. 5 and 6) on the extent of the reaction of sulphite with silver bromide during sensitizing.

Unless the constant rate is entirely the result of compensation changes, which is rather improbable for the range of conditions used, it indicates that the rate is relatively independent of bromide-ion concentration when the latter is low enough. The experiments in which bromide was added to the reaction mixture before the start of the reaction confirm this. Inspection of table 1 shows that in reactions with unprotected silver bromide and 0.010 N Na_2SO_3 , the maximum rate was 0.48 for an initial $[\text{Br}^-]$ 7×10^{-7} and 0.57 for an initial $[\text{Br}^-]$ 7.7×10^{-5} . In the presence of gelatin, with the same sulphite concentration, an increase in initial $[\text{Br}^-]$ from 4×10^{-6} to 3.8×10^{-4} decreased the rate only from 0.19 to 0.10. At $10^{-3} N$, however, reaction was practically stopped. This agrees with the photographic evidence (3), that ripening was very slow even at 65 C pH 7.3 and 0.15 N Na_2SO_3 when the bromide-ion concentration was $5.6 \times 10^{-3} N$.

² A sulphite solution held in the apparatus for 4½ hours under the conditions of a reaction decreased in titre from 0.00095 to 0.00090 N in that time, indicating that the protection from air was adequate. A suspension of silver bromide in the (deactivated) gelatin was held under hydrogen at 73.40 C for 5½ hours; the reaction in the absence of sulphite increased the bromide-ion concentration only from 2.0×10^{-5} to $3.4 \times 10^{-5} N$.

The rate of reaction increased less rapidly than the concentration of sulphite, which is in agreement with the photographic results (3, figs. 4, 5, 6). The data on the effect of hydrogen-ion concentration are approximate only, but indicate that it was of the same order as its effect on photographic sensitization by sulphite (3, fig. 8). This is less than for after-ripening with active gelatin (5) and much less than for the thiocarbamide reaction (next section).

TABLE 1.—*Reaction of sodium sulphite with silver bromide at 73.4 C*

[The induction period is the time required to reach the maximum reaction rate]

Na ₂ SO ₃ concn. N	Colloid	pH	[Br] ×10 ⁴ at start	Induc- tion period	Maximum rate, milli- equivalents Br- formed per hour per liter	Remarks
				Hours		
0. 0102	None-----	9.0	0. 007	2 ¹ / ₄	0. 38	Exposed to light.
. 0102	do-----	9.0	. 007	2 ¹ / ₄	. 48	
. 0105	do-----	9.0	. 004	2 ¹ / ₄	. 47	
. 00089	do-----	8.7	. 006	1 ¹ / ₂	. 15	
. 0103	do-----	9.0	. 77	2 ¹ / ₄	. 57	
. 0102	do-----	9.0	9. 4	>2	. 0	
. 0112	Gum arabic--	8.5+	0. 24	2 ¹ / ₄	. 24	
. 0103	Gelatin-----	8.5	0. 024	1 ¹ / ₂	. 17	
. 0105	do-----	7.8	. 037	1 ¹ / ₂	. 17	
. 0101	do-----	-----	. 045	3 ¹ / ₄	. 20	pH determined at end of reaction. Made with different gelatin from others; por- tions of same emulsion; second portion exposed to light.
. 0098	do-----	-----	. 040	3 ¹ / ₄	. 18	
. 0030	do-----	8.0	. 034	1 ¹ / ₂	. 091	Emulsion incompletely washed. pH determined at end of reaction. Do.
. 0012	do-----	8.4	. 31	1 ¹ / ₂	. 031	
. 0101	do-----	6.8	. 12	1 ¹ / ₂	. 13	
. 0102	do-----	6.2	. 06	1 ¹ / ₂	. 11	
. 0099	do-----	8.6	3. 8	2 ¹ / ₄	. 10	

The induction period of the reaction was lengthened by protective colloids. Gum arabic was less effective than half the amount of gelatin, which is in accordance with their relative ratings as protective colloids. At 73.4 C the colloids appeared to decrease the maximum rate of reaction; the reaction mixtures with and without colloids unfortunately were not otherwise identical, but the differences in bromide and hydrogen-ion concentrations do not appear sufficient to explain the differences in rate.

The existence of the induction period indicates that the reaction is autocatalytic, and therefore presumably takes place at the surface of the new solid phase. It should, then, be accelerated by adding silver. The data of table 1 show that exposure of the silver bromide to light was not sufficient to accelerate the reaction. A new series³ of experiments were made with special reference to the autocatalysis. The temperature was raised to 88.2 C so that the reactions could be carried nearer completion in the time available for each run. The reaction mixtures were buffered to pH 6.7 with N/2 sodium acetate-acetic acid mixture (see table 2) to simplify the kinetics by minimizing the change in pH during the reaction; this, however, tended to coagulate the silver bromide. The data were less regular, probably for this reason.

³ The first series was intended as a preliminary survey, which would be continued after obtaining comparative results with allyl thiocarbamide. This became impossible so the second series was limited as indicated.

TABLE 2.—*Buffer solutions used for reaction mixtures of allyl thiocarbamide and silver bromide*

[410 ml water and 62.5 ml of 4 *M* sodium acetate, to which was added 0.050 *N* acetic acid, as follows. pH determined with hydrogen electrode at 30.0 C]

MI HAc solution-----	5.0	10.0	15.0	23.0	27.5	40.0	60.0
pH-----	7.64	7.29	7.11	6.92	6.84	6.67	6.48

The tenth-normal sodium acetate buffer contained 5.0 ml of 0.050 *N* HAc and 12.5 ml 4 *M* NaAc in 500 ml; pH 6.77.

Figure 1 represents the results of these experiments. Curves 1 and 4 show the typical course of the reaction without catalyst. In

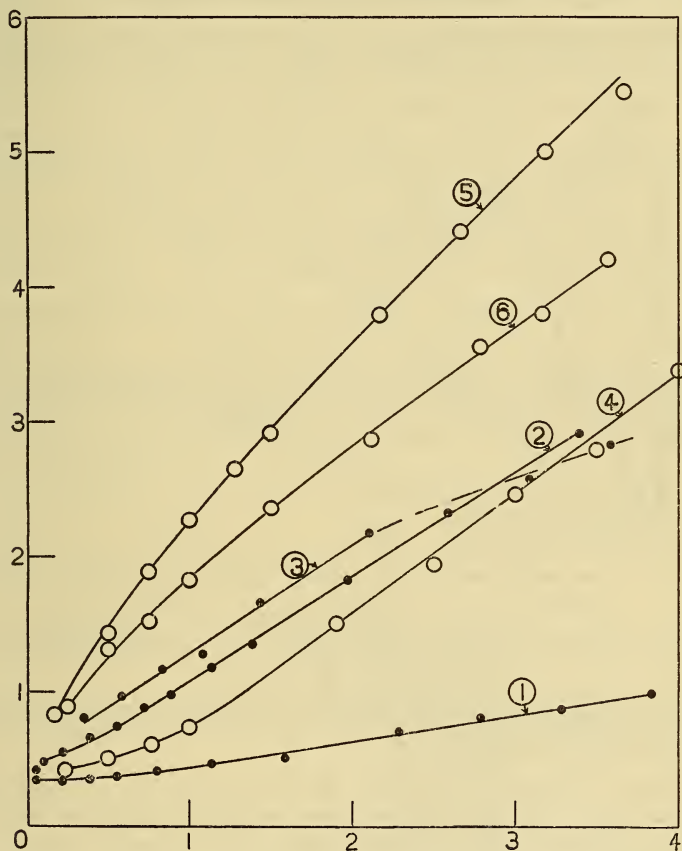


FIGURE 1.—Rate of reaction between silver bromide and sodium sulphite solutions at 88.2 C.

Abscissas, time in hours; ordinates, bromide-ion concentration of solution, $\times 10^4$. Curves 1, 2, and 3 for 0.0012 *N* Na_2SO_3 , curves 4, 5, and 6 for 0.0033 *N* Na_2SO_3 . Curves 1 and 4, silver bromide suspended in 1 percent gelatin. Curves 2 and 5, silver bromide plus silver, suspended in 1 percent gelatin. Curves 3 and 6, silver bromide plus silver, without protective colloid.

the other experiments, colloidal silver was added before the sulphite. It was prepared by allowing the silver bromide to react with sodium sulphite, then washing thoroughly by decantation before using it for the kinetic experiment.⁴ Approximately one half milli-equivalent

⁴ The product was a brown absorption compound, from which the silver could not be removed completely by nitric acid.

of metallic silver was added to one half liter of reaction mixture. The curves show clearly that the induction period was completely eliminated by the addition of the silver. The order of the reaction remained less than one. As in the other series, the rate began to decrease irregularly in the unprotected mixtures after a relatively short interval. In the presence of sufficient silver, the maximum rate was apparently the same with and without gelatin.

III. THE REACTION OF SILVER BROMIDE WITH ALLYL THIOCARBAMIDE

1. EXPERIMENTAL METHODS

Preliminary experiments showed that this reaction is many times faster than that with sulphite under the same conditions. The

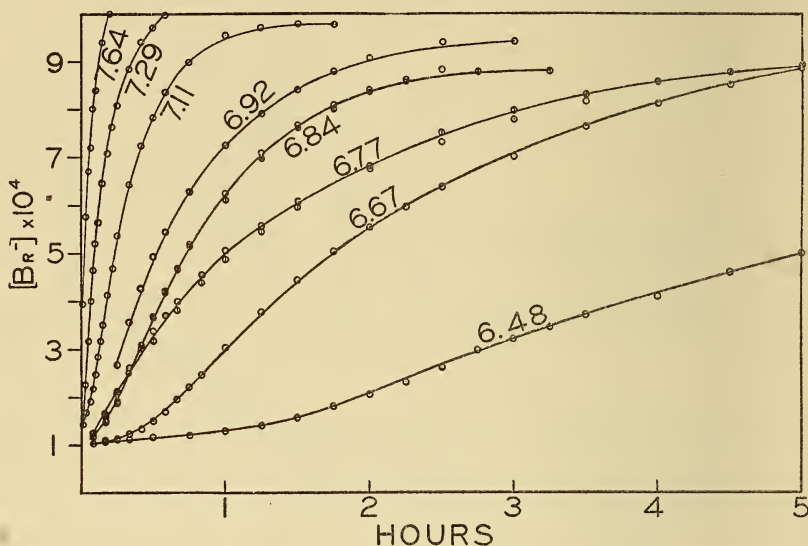


FIGURE 2.—The reaction between silver bromide and 1.00×10^{-3} N allyl thiocarbamide solutions at 30.0 C.

Abcissas, time from start of reaction; ordinates, bromide-ion activities, which are a direct measure of the reaction which has taken place. Numbers on the curves give the pH. All buffered with NaAc-HAc mixtures; 0.1 N for pH 6.77 and 0.5 N for the others. No protective colloid except for the runs at pH 6.84 which were made in a gelatin emulsion.

temperature of 30.0 C used for the determination of bromide-ion concentrations with the silver-silver bromide electrode proved to give convenient reaction velocities, and the electrode adapted itself so rapidly to the solution that it was found possible to run the reactions in the air thermostat used for the electrode measurements, the silver electrode and salt bridge being left in place throughout the reaction. This arrangement had the great advantage that readings could be taken almost continuously when needed.

The electrode was coated with silver sulphide at the end of a run, but continued to give normal readings in known bromide solutions. In the few cases where the electrode gave trouble it was quite obvious from the erratic nature of the potential. The window of the thermostat was coated with orange lacquer which excluded practically all

light of less than 500m μ wave length, but as a further precaution a black curtain was kept over it. The silver bromide was necessarily exposed to light in setting up the apparatus, but the results with sulphite indicate that this was not likely to affect the reaction.

As this reaction was known in advance to be sensitive to hydrogen-ion concentration, all the reaction mixtures were buffered. Tenth normal ammonium acetate was used in some of the runs; the pH was 6.68 at first, falling to about 6.5 on completing reaction with 0.001 *N* allyl thiocarbamide. Acetic acid-sodium acetate mixtures were adopted later; compositions of the mixtures and pH determined at 30.0 C with the hydrogen electrode are given in table 2. In using these, the acetic acid was first added to the silver bromide suspension, then the thiocarbamide; no reaction took place in the presence of the acetic acid and the mixture could be brought to equilibrium before the reaction was started by adding the concentrated (4 *M*) solution of sodium acetate. The final addition took about 60 seconds, the mixture being rapidly stirred with a turbine stirrer.

The original data on the effect of pH on reaction velocity are plotted in figure 2 to illustrate the general form of the curves. After an extended induction period, the reaction usually follows the first order equation closely enough so that the constant can be used to characterize the velocity. This is illustrated by the data given in table 3.

TABLE 3.—Original data of reaction between silver bromide (with no protective colloid) and allyl thiocarbamide

[0.03 mol AgBr suspended in 477 ml water at 30.0 C, plus 5.0 ml 0.050 *N* HAc. Then added 5.0 ml 0.100 *N* allyl thiocarbamide solution and allowed mixture to reach equilibrium with electrode. Reaction started by adding 12.5 ml of 4.0 *M* NaAc solution, raising pH to 6.77; time taken from this. Velocity constants calculated from the equation $K = \frac{2.303}{t} \log \frac{a}{a-x}$ where *a* is the initial concentration of allyl thiocarbamide and *x* is the concentration at time *t*]

Time	emf of cell	Bromide-ion activity <i>N</i>	Reaction	$k \times 10^3$
<i>Minutes</i>			<i>Percent</i>	
Before addition.....atc	-0.0968	1.08×10^{-6}	-----	-----
After addition.....atc	+ .0125	7.09×10^{-5}	-----	-----
After addition NaAc.....0	.0221	1.02×10^{-4}	0.	
5	.0258	1.18×10^{-4}	2.1	4.
10	.0345	1.65×10^{-4}	8.1	8.7
15	.0411	2.12×10^{-4}	14.3	10.4
20	.0467	2.63×10^{-4}	20.8	11.7
25	.0502	3.01×10^{-4}	25.8	12.0
30	.0533	3.38×10^{-4}	30.6	12.2
35	.0557	3.71×10^{-4}	34.9	12.2
40	.0577	4.00×10^{-4}	38.7	12.2
50	.0611	4.56×10^{-4}	45.9	12.3
60	.0638	5.06×10^{-4}	52.2	12.3
75	.0664	5.59×10^{-4}	59.0	11.9
90	.0686	6.08×10^{-4}	65.5	11.9
120	.0713	6.75×10^{-4}	74.1	11.3
150	.0734	7.31×10^{-4}	81.3	11.3
180	.0750	7.80×10^{-4}	87.9	11.8

¹ Concentrations of allyl thiocarbamide have been expressed in terms of normality with respect to silver. Thus, 0.10 *N* = 0.05 *M*. This does not affect the velocity constant, but comes into the equilibrium equations.

Independent evidence of the influence of some of the variables was obtained by a different method of following the reaction. In these experiments the bromide-ion activity was held constant by addition of 0.0100 *N* silver nitrate solution and the rate of reaction measured by the necessary rate of addition of the silver. A turbine stirrer

operated as rapidly as possible without splashing was used to mix the silver solution with the suspension. If the flow of solution was temporarily interrupted it was very evident from the rate of change of electrode potential that the rate of reaction with the silver bromide corresponded to the rate of addition of solution which had been required. These experiments gave particularly clear evidence of the autocatalytic nature of the reaction. For example, the data of curve 4, figure 3, were plotted on a large scale and the slope of the curve, giving the instantaneous rate of reaction, carefully measured at each

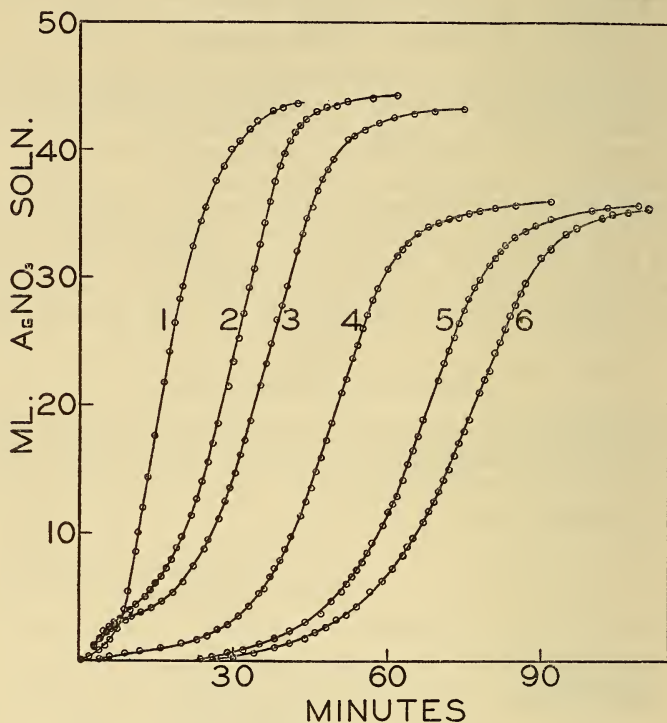


FIGURE 3.—The reaction between silver bromide and allyl thiocarbamide at 30.0 C and constant bromide-ion concentration.

pH maintained at 6.84 by 0.5 *N* NaAc—HAc buffer. Conditions for the runs are given under the corresponding numbers in table 5. As all those illustrated were made with 0.5 liter of 1.00×10^{-3} *N* allyl thiocarbamide, 50 ml of the AgNO_3 solution would represent complete reaction.

ml addition. Up to 10 ml, 20 percent reaction, the rate of reaction was proportional within 5 percent to the percentage reaction, after which it rapidly approached a constant value.

The results of this series were obviously not as reproducible as the others; they were probably much more dependent on mechanical details such as the mixing of the solution. It will be noted, however, from table 5 that the maximum rate of reaction and the fraction of the total occupied by the induction period were reasonably constant for given conditions; the greatest variation was in the time of the induction period which appears to be less significant. It will also be noted that these reactions did not run to completion like the others, and that the reactions in the emulsion were the least complete.

2. VARIABLES AFFECTING THE RATE OF REACTION

The curves shown in figure 3 indicate that the reaction is autocatalytic. It was readily demonstrated that silver sulphide is the catalyst. The mixture of silver bromide and silver sulphide left from a previous reaction was thoroughly washed and used to make up the suspension for a new experiment, the conditions otherwise being the same as those given in table 3. The reaction between the allyl thiocarbamide and the silver bromide-silver sulphide mixture started at the maximum rate (3 percent per minute) with no induction period, and followed approximately the equation

$$\frac{d[Br]}{dt} = k \cdot \frac{a-x}{[Br^-]}$$

In another experiment, colloidal silver sulphide was prepared by decomposition of sodium thiosulphate in the presence of gelatin. This was added to a Lippmann emulsion which had previously been found to react with allyl thiocarbamide in the absence of catalyst only after a long induction period. With the addition of the colloidal silver sulphide, there was no induction period and the reaction was even more rapid than in the previous experiment with unprotected silver bromide-silver sulphide mixture. It should be noted that in this second case it is very improbable that the silver bromide and silver sulphide were in contact. Silver bromide carrying colloidal silver from a previous reaction with sodium sulphite reacted at a normal rate with allyl thiocarbamide, indicating that the catalysis by silver sulphide is specific.

Calculation from the data given in figure 2 indicates that the rate of reaction varies inversely as the square of the hydrogen-ion concentration, as a first approximation. Velocity constants could not be calculated for the more rapid reactions, so the slopes of the curves at $[Br^-] 3.5 \times 10^{-4}$ were taken as the rate for this estimate. At pH 4.7 no reaction can be detected for several hours; the practical limit lies about at Sheppard's original figure of pH 6. The effect of acid on the reaction is therefore even greater than on after-ripening with active gelatin (5). After-ripening is quite appreciable at pH 5, which indicates the presence of sensitizers other than allyl thiocarbamide in gelatin.

The reaction velocity varied approximately as $\frac{1}{[Br^-]^{3/2}}$.

This relation may be obtained either from the maximum velocities of the reaction at constant $[Br^-]$, or from the constants of table 4. This is much greater than the effect of bromide-ion concentration on photographic after-ripening (6).

The last three experiments listed in table 5 indicate that the rate of reaction is directly proportional to the concentration of allyl thiocarbamide, the maximum rates corresponding to about the same percentage of the original concentration in each case. The run with 3×10^{-3} *N* allyl thiocarbamide, corrected for the increased bromide-ion concentration, comes within 20 percent of the same ratio.

TABLE 4.—*Velocity of reactions of silver bromide with allyl thiocarbamide, buffered by 0.10 N ammonium acetate, without protective colloid, at 30.0 C.*

[0.03 mol silver bromide per liter of reaction mixture. Initial pH 6.68]

Initial concentration of allyl thiocarbamide <i>N</i>	Initial bromide-ion activity <i>N</i>	<i>k</i> × 10 ³	Initial concentration of allyl thiocarbamide <i>N</i>	Initial bromide-ion activity <i>N</i>	<i>k</i> × 10 ³
3.00 × 10 ⁻⁴	6.5 × 10 ⁻⁵	20.1	1.00 × 10 ⁻³	1.66 × 10 ⁻⁴	6.4
1.00 × 10 ⁻³	9.7 × 10 ⁻⁵	9.6	1.00 × 10 ⁻³	1.6 × 10 ⁻⁴	6.3
1.00 × 10 ⁻³	9.6 × 10 ⁻⁵	10.5	1.00 × 10 ⁻³	2.4 × 10 ⁻⁴	2.25
1.00 × 10 ⁻³	9.6 × 10 ⁻⁵	11.3	1.00 × 10 ⁻³	3.1 × 10 ⁻⁴	1.57
3.00 × 10 ⁻³	2.7 × 10 ⁻⁴	1.41	1.00 × 10 ⁻³	3.4 × 10 ⁻⁴	1.6

TABLE 5.—*Reaction velocities at constant bromide-ion concentration*[All experiments at 30.0 C, pH 6.84 (0.5 *N* HAc—NaAc buffer), 0.03 g equivalent of silver bromide per liter of reaction mixture]

Curve number in fig. 3	[Br ⁻]	Allyl thiocarbamide concentration <i>N</i>	Maximum velocity milliequivalents per hour per liter	Induction period		Remarks
				Percent of reaction	Minutes	
1-----	3.1 × 10 ⁻⁴	1.00 × 10 ⁻³	2.8	10	9½	No protective colloid.
	2.4 × 10 ⁻⁴	1.02 × 10 ⁻³	7.7	30	12½	Do.
2-----	3.1 × 10 ⁻⁴	1.00 × 10 ⁻³	2.05	28	24	{ Silver bromide precipitated and washed before suspending in gelatin.
3-----	3.1 × 10 ⁻⁴	1.00 × 10 ⁻³	1.75	30	30	
	3.1 × 10 ⁻⁴	1.00 × 10 ⁻³	3.0	35	29	{ Emulsion made by adding silver nitrate solution rapidly in small portions.
	3.1 × 10 ⁻⁴	1.00 × 10 ⁻³	1.75	40	40	
	3.1 × 10 ⁻⁴	1.00 × 10 ⁻³	.02	-----	> 1,000	{ Lippman type ("grainless") emulsion.
4-----	3.1 × 10 ⁻⁴	1.00 × 10 ⁻³	1.45	24	35	
5-----	3.1 × 10 ⁻⁴	1.00 × 10 ⁻³	1.35	26	59	{ Emulsion, made by adding silver nitrate solution in continuous fine stream for 10 minutes.
6-----	3.1 × 10 ⁻⁴	1.00 × 10 ⁻³	1.15	27	70	
	1.2 × 10 ⁻⁴	1.00 × 10 ⁻³	5.5	35	12	{ Emulsion made by adding silver nitrate in continuous fine stream.
	3.6 × 10 ⁻⁴	3.00 × 10 ⁻³	2.6	23	45	
	2.6 × 10 ⁻⁴	0.51 × 10 ⁻³	0.98	40	36	
	2.5 × 10 ⁻⁴	1.02 × 10 ⁻³	1.93	30	40	
	3.0 × 10 ⁻⁴	2.04 × 10 ⁻³	3.36	30	54	

The rates of reaction for the experiments listed in table 4 have been characterized by the "constants" obtained from the first order equation, as in table 3. These were found to be dependent on the initial bromide-ion concentration; it will be noted that the constant was practically the same for an initial [Br⁻] of 3 × 10⁻³ in the cases where this represented simply the solubility of AgBr in 3 × 10⁻³ *N* thiocarbamide, and where the reaction mixture contained 1 × 10⁻³ *N* thiocarbamide plus soluble bromide.

The apparent first order of the reaction was obviously the result of compensation between the autocatalysis and the factors decreasing the rate of reaction. The rate of reaction during the period of autocatalysis may possibly be expressed by thus:

$$-\frac{dx}{dt} = k \frac{(a-x)x}{[\text{Br}^-]^n},$$

the *x* in the numerator corresponding to the autocatalytic factor. If *n* is close to 1, and [Br⁻] is proportional to *x*, as in reactions starting

with pure silver bromide and allyl thiocarbamide, this reduces to a pseudo first order. If soluble bromide had been added to the reaction mixture before starting, $[\text{Br}^-]$ was no longer proportional to x and it was observed that the first-order equation fitted less closely.

An unexpected and important feature of the data was that the reaction velocity proved to be independent of the amount of silver bromide present. Ordinarily the silver bromide was equivalent to nearly 30 times the allyl thiocarbamide. When this ratio was reduced to 2.6, the results of a run without gelatin, buffered with ammonium acetate, checked the previous data within the limit of reproducibility. The experiment was repeated using an "emulsion" of silver bromide in gelatin. The excess in one case was reduced to 5 percent, gelatin being added to keep the concentration 1 percent both in this run and in the control with 2,600 percent excess AgBr. The difference between the two was so small as to be doubtful.

The effect of gelatin is not as large in this reaction as in the one with sulphite. It is most evident as an increase in the induction period. In the extreme case of the "grainless" emulsion recorded in table 5 there was no measurable reaction in 15 hours. Another very fine-grained emulsion required 30 minutes to react as much as a normal emulsion in 5 minutes under the same conditions; once under way, the "constants" were about the same as in the normal emulsion.⁴ The curve for pH 6.84 in figure 2 was obtained with gelatin emulsions, and falls in well with the others which were made with unprotected silver bromide, although there is a possible difference in induction period. The effect of the gelatin on induction period is also evident in the curves for reaction at constant $[\text{Br}^-]$, figure 3; here there is also a definite effect on the rate of reaction after the induction period.

IV. ADSORPTION AND SOLUBILITY DATA

1. ADSORPTION OF POTASSIUM BROMIDE TO SILVER BROMIDE

Silver bromide was known to adsorb soluble bromides, but no quantitative data were available for the region involved in these reactions. They were obtained by the use of the electrode, the bromide-ion concentration in suspensions of silver bromide being determined after successive additions of potassium bromide solution. The silver bromide used for the experiments was precipitated at room temperature from 0.5 *N* solutions of silver nitrate and potassium bromide, the latter being 10 percent in excess to prevent precipitation of the trace of chloride which persists through repeated recrystallization of the bromide. The precipitate was washed with 15 portions of hot distilled water; its suspension before adding soluble bromide gave a bromide-ion concentration within ± 5 percent of the value calculated from the solubility product of silver bromide at 30 C. The data are presented graphically in figure 4 as g mols of KBr per g mol of AgBr; this ratio may be converted to the weight basis by multiplying by 0.58.

⁴ It was not possible to determine whether a "grainless" emulsion would react normally with sulphite, as a highly transparent washed emulsion of this type became opaque after a few minutes at 88 C, indicating a coagulation.

2. SOLUBILITY OF SILVER BROMIDE IN SODIUM SULPHITE SOLUTIONS

The solubility of the silver bromide in the sodium sulphite solutions at 30.0 C could be estimated from the original electrode readings in the reaction mixtures, since the bromide-ion concentration (corrected for the solubility of silver bromide in pure water) was equal to the dissolved silver bromide. In 0.010 N Na_2SO_3 (pH 8.5) the silver bromide was $7.5 \pm 0.5 \times 10^{-5} N$; this was reduced to $3.5 \times 10^{-5} N$ in a gelatin emulsion at pH 6.2 with the same sulphite concentration, and to $4 \times 10^{-5} N$ by the addition of $4 \times 10^{-4} N$ KBr at pH 8.5. The solubility in 0.0030 N Na_2SO_3 was 2.9×10^{-5} , and in 0.0012 N , 2.0×10^{-5} . These figures are about double the values of Mees and Piper (7) obtained by analysis at room temperature. At the reaction temperatures the solubility was probably several times as great, but

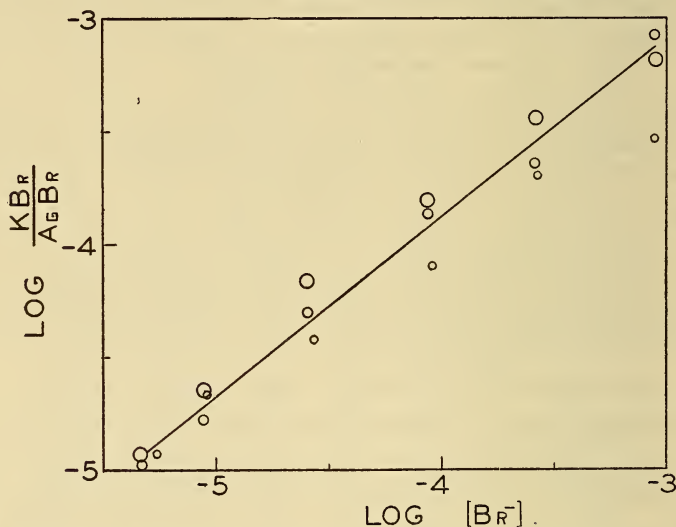


FIGURE 4.—Adsorption of KBr by $AgBr$, in the absence of gelatin, at 30.0 C. The different size circles indicate separate series of measurements.

the variation with concentration of sulphite, and hydrogen and bromide ions may be expected to be parallel to the results at lower temperature.

No data on the adsorption of sulphite to silver bromide were obtained.

3. SOLUBILITY OF SILVER BROMIDE IN ALLYL THIOCARBAMIDE SOLUTIONS

The available data on the solubility of silver bromide in allyl thiocarbamide solutions do not cover the range of concentrations used in our experiments or the equilibrium relations. Pawelka (8) measured the equilibrium between silver ion and thiocarbamide electrometrically and found that the complex ion consisted of three molecules of the latter to one silver ion. The data of table 6 indicates that when there is a sufficient excess of allyl thiocarbamide over silver, the complex ion is $Ag(ate)_3^+$, but that as the concentration of silver is increased more and more of the 1:1 ion is formed.

In dilute solutions of allyl thiocarbamide saturated with silver bromide the thiocarbamide-silver ratio is such that the 1:2 ion is still the principal form. When silver bromide goes into solution in a solution of allyl thiocarbamide, bromide ions and complex silver-thiocarbamide ions must be formed in equal numbers. Their normalities will therefore be equal, provided the solubility of silver bromide in pure water may be neglected. The concentration of dissolved silver bromide may thus be determined simply by electrometric measurement of $[Br^-]$ in the solution.

TABLE 6.—Equilibrium in allyl thiocarbamide, silver-nitrate mixtures at 30.0 C, pH 3.34

[Constants calculated from the equation $K = \frac{[Ag^+] \times [atc]^2}{[Ag(atc)_2^+]}$]

AgNO ₃ , N	Allyl thiocarbamide N	[Ag ⁺]	K
2.71×10 ⁻³	2.17×10 ⁻²	2.47×10 ⁻¹²	4.24×10 ⁻¹¹
5.42×10 ⁻³	2.16×10 ⁻²	4.68×10 ⁻¹²	4.00×10 ⁻¹¹
1.07×10 ⁻⁴	2.15×10 ⁻²	9.71×10 ⁻¹²	4.15×10 ⁻¹¹
2.13×10 ⁻⁴	2.13×10 ⁻²	2.10×10 ⁻¹¹	4.32×10 ⁻¹¹
4.17×10 ⁻⁴	2.08×10 ⁻²	5.49×10 ⁻¹¹	5.25×10 ⁻¹¹
8.00×10 ⁻⁴	2.00×10 ⁻²	1.21×10 ⁻¹⁰	5.10×10 ⁻¹¹
1.48×10 ⁻³	1.85×10 ⁻²	4.50×10 ⁻¹⁰	7.20×10 ⁻¹¹
1.86×10 ⁻³	1.77×10 ⁻²	9.40×10 ⁻¹⁰	9.9×10 ⁻¹¹
2.21×10 ⁻³	1.70×10 ⁻²	2.00×10 ⁻⁹	14.2×10 ⁻¹¹
2.52×10 ⁻³	1.63×10 ⁻²	4.02×10 ⁻⁹	20.2×10 ⁻¹¹

Under conditions where only a single species of complex ion is formed, the solubility relations are quite simple. We have, first, that

$$[Ag(atc)_2^+] = [Br^-]. \quad (1)$$

Since

$$[Ag^+] \times [Br^-] = S_{AgBr}, \quad (2)$$

we may make the substitutions

$$\frac{[Ag^+] \times [atc]^2}{[Ag(atc)_2^+]} = K = \frac{S \times [atc]^2}{[Br^-] \times [Ag(atc)_2^+]} \quad (3)$$

$$\frac{[atc]^2}{[Ag(atc)_2^+]} = \frac{K}{S} \text{ or } \frac{[atc]}{Ag(atc)_2^+} = K^1 \quad (4)$$

Thus the ratio of free allyl thiocarbamide to the complex ion is a constant and, as a first approximation, the solubility of silver bromide is directly proportional to the total concentration of allyl thiocarbamide. Figure 5 shows how well this relation holds for the range of concentrations used in the velocity experiments. At pH 3.3 (0.005 N HAc), the solutions were quite stable, so that the equilibrium measurements could be made without difficulty. The upper limit at which solubility could be measured was about pH 6.8, and the data in figure 5 at pH 6.49 and the lower concentrations are possibly in error from reaction in the solution. As already mentioned, the more concentrated solutions are the slower to react because of their higher bromide ion concentration.

The solubility increased rapidly with pH. K in equation 3 fell from 15.4×10^{-11} at pH 3.34 to 3.0×10^{-11} at pH 6.77. Assuming that

the formation of the complex ion is dependent on the presence of free amino groups in the allyl thiocarbamide, this is evidence for the "zwitterion" theory of its structure.

In mixtures of allyl thiocarbamide and soluble bromide, equation 3 should hold, but not equation 4. Mixtures of allyl thiocarbamide and soluble bromide, in buffer solution at pH 6.77, were made up and saturated with silver bromide. It was found that the solubility was roughly proportional to the thiocarbamide concentration, in spite of the addition of soluble bromide. (The measurements of solubility in this case were less accurate, since the solutions were unstable and the increase in $[\text{Br}^-]$ on adding the AgBr was small.) Since part of

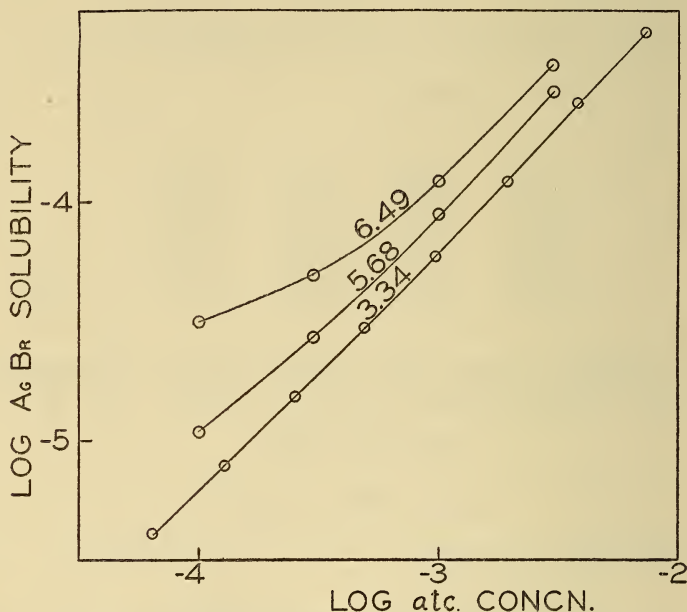


FIGURE 5.—Solubility of silver bromide in solutions of allyl thiocarbamide at 30.0 C. Numbers on the curves give the pH; 0.005 N HAc only was used for pH 3.34 and 0.5 N NaAc—HAc mixtures for the others.

the bromide-ion concentration in the reaction mixture came from dissolved silver bromide, it was necessary to subtract this amount from the total in order to get the amount which came from the product of the reaction; the amount subtracted being under 10 percent, an approximate correction was satisfactory.

A few experiments were completed on the adsorption of allyl thiocarbamide on silver bromide. The thiocarbamide solutions (in $1.0 \times 10^{-4} N$ H_2SO_4 , pH 4.7) were stirred with silver bromide prepared as for the experiments on adsorption of soluble bromide, and the change in concentration determined. The conditions chosen were not satisfactory, but in $5.0 \times 10^{-4} M$ allyl thiocarbamide ($1.00 \times 10^{-3} N$), 1×10^{-3} mol was adsorbed on 1 mol of AgBr ; at $2.9 \times 10^{-4} M$, the adsorption per mol AgBr was 4×10^{-4} . These values are approximately double the corresponding ratios for KBr on AgBr .

V. DISCUSSION

To the best of our knowledge the only other studies of the kinetics of reactions in which a solid phase reacts with a solution to form a new solid phase have also been in connection with a photographic problem, that of development (9). Our experimental methods show promise of being applicable to development as well as to sensitizer reactions.

Complete mathematical analysis of the kinetics of the reactions which we have studied would be extremely difficult in any case, but even with the limited data available it is possible to draw a few definite conclusions. The reaction with allyl thiocarbamide will be considered first because more information is available. Under the conditions of our experiments the first step must have been the formation of the complex ion in solution. It could not have proceeded by adsorption of allyl thiocarbamide to silver bromide followed by a slower rearrangement of the adsorption complex, since the rate was practically independent of the amount of silver bromide. Furthermore, colloidal silver sulphide, added separately from the silver bromide under conditions which preclude its adsorption by the latter, catalyzed the reaction so strongly that it evidently takes place at the silver sulphide surface and is not restricted to the silver sulphide-silver bromide interface. These statements are for the conditions of our experiments, and do not necessarily apply to conditions in the emulsion with a much lower concentration of allyl thiocarbamide. In the emulsion, the ratio of adsorbed sensitizer to sensitizer in solution is probably greater than one; in our experiments it was less than one. However, it seems probable that the reactivity of the material in solution is considerably greater than that of the material adsorbed on silver bromide. Solutions of silver halides in allyl thiocarbamide, like those in sodium thiosulphate, are stable only in the presence of a large excess of the solvent. Under the conditions of sensitization, the solution is continually saturated with silver bromide and hence at its minimum stability. It seems possible that even in the emulsion the reaction may go on by decomposition of the solution.

The data on kinetics are not sufficient to formulate any mechanism consistent with the chemistry of the system. It may be noted that two hydrogen ions must be liberated by the decomposition of the silver bromide-thiocarbamide complex to form one Ag_2S , so that the reaction would be expected to be highly sensitive to hydrogen-ion concentration. The bromide ions, liberated when the complex ion was formed, affect the velocity through their effect on the solubility equilibrium.

The effect of the gelatin on the catalysis of the reaction by silver sulphide cannot be satisfactorily explained. If there were only the case of the "grainless" emulsions, it would appear that the gelatin simply retarded the crystallization of silver sulphide. The effect of the gelatin, however, nearly vanished in the normal emulsions, although the total gelatin concentration was the same.

The kinetic data on the sulphite reaction leave its mechanism in doubt. The low apparent order is rather remarkable, since by any conceivable mechanism hydrogen ions must be formed in the final step, and the equilibrium in solution must be dependent on bromide-ion concentration. The effect of gelatin on reaction velocity is consistent with its known tendency to retard the crystallization of silver

from solution. The reaction was catalyzed by metallic silver. This has already been observed (10) (11) in the precipitation of silver from solutions of silver sulphite in sodium sulphite. The probability that the reaction takes place at the solid silver bromide in preference to the dissolved silver salts seems small; there was no evidence that the rate of reaction was dependent on the amount of solid silver bromide. Since photographic sensitization was obtained under conditions only slightly removed from those of our kinetic experiments, it appears very probable that sensitization was produced by precipitation of silver on the silver bromide from the solution phase.

We have already pointed out (6) that the photographic evidence on after-ripening suggests that the formation of sensitivity nuclei is an autocatalytic process. The data in this paper show that this is actually the case. Furthermore, it seems possible that the autocatalysis is a necessary condition for sensitization. If it exists, the silver sulphide or silver will tend to build up on the first particles formed, decreasing the number and increasing the average size of the nuclei. Reinders and Hamburger have recently calculated the probabilities of a purely random distribution of silver sulphide over the surface of silver bromide grains in the quantities involved in sensitization, showing that aggregates as large as 3 or 4 molecules would be of very infrequent occurrence. They have presented evidence which they have interpreted to show that, under favorable conditions, aggregates of this size may serve as centers for physical development. However, the random distribution seems probable only for instantaneous ionic reactions such as that with sodium sulphide, which does not produce sensitization. We therefore suggest that autocatalytic reactions, such as those with allyl thiocarbamide or sodium sulphite, favor sensitization because they avoid the relatively uniform distribution of silver sulphide or silver which is characteristic of instantaneous ionic reactions. Sheppard's observation that the sensitizers must form molecular complexes with the silver halides has been supported by the discovery of the sensitizing property of sodium sulphite. Our interpretation of the necessity for this condition is different from that of Sheppard. We believe that it is characteristic of sensitizers because it is characteristic of slow, autocatalytic reactions as contrasted to instantaneous ionic reactions.

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